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(54) Title: CATALYTIC CRACKING FOR OLEFIN PRODUCTION (57) Abstract Heavy hydrocarbon feeds are catalytically cracked to lighter products by contacting with a catalyst containing large pore molecular sieve component and ZSM-5 and/or ZSM-11, the catalyst having a substantially inert matrix material such as silica and/or clay and having active matrix material of less than 10 wt.% based on total catalyst composition. The products include light olefins ethylene and propylene, and the light olefin yield is increased when the matrix material is substantially inert.		

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CATALYTIC CRACKING FOR OLEFIN PRODUCTION

The present invention relates to the catalytic cracking of heavy hydrocarbon feeds over a catalyst to produce hydrocarbon compounds of lower molecular weight including, especially, light olefins such as ethylene and propylene. The catalyst includes an intermediate pore size zeolite in a substantially inert matrix; a large pore molecular sieve may also be present.

Gasoline is the traditional high value product of fluid catalytic cracking (FCC). Currently however, ethylene and propylene are in higher demand and have higher value per pound than does gasoline. In conventional fluid catalytic cracking, typically less than 2 wt.% ethylene in dry gas is obtained, and it is used as fuel gas. The propylene yield is typically 3-6 wt.%.

Catalytic cracking operations are commercially employed in the petroleum refining industry to produce useful products, such as high quality gasoline and fuel oils from hydrocarbon - containing feeds. The endothermic catalytic cracking of hydrocarbons is most commonly practiced using Fluid Catalytic Cracking (FCC) which has replaced the older moving bed catalytic cracking process. In FCC, the cracking catalyst circulates cyclically between a cracking reactor and a catalyst regenerator. In the cracking reactor, hydrocarbon feedstock is contacted with hot, active, solid particulate catalyst in the absence of added hydrogen, for example at pressures up to 50 psig (4.4 bar) and temperatures typically from 425°C to 600°C. As the hydrocarbon feed is cracked to form more valuable products, a carbonaceous residue known as coke is deposited on the catalyst, deactivating the catalyst. The cracked products are separated from the coked catalyst, the coked catalyst is stripped of volatiles, usually with steam in a catalyst stripper, after which the catalyst is regenerated. Decoking restores catalyst activity while the burning of the coke heats the catalyst. The heated, regenerated catalyst is recycled to the cracking reactor to crack more feed.

The trend in FCC has been to dilute phase riser cracking with a brief hydrocarbon feed residence time of one to ten seconds. In this method, a small amount of diluent, e.g., steam up to 5 wt.% of the feed, is added to the feed at the bottom of the riser. The FCC process generally uses a cracking catalyst which includes a large pore zeolite such as USY or REY as the active cracking component. The octane rating of the cracked FCC gasoline may be increased by the addition of a minor amount of

ZSM-5 to the catalyst inventory, with commercial units believed to operate with less than 10 wt. % additive, usually considerably less.

U.S. Patent No. 5, 389,232 (Adewuyi) describes an FCC process in which the catalyst contains up to 90 wt.% conventional large pore cracking catalyst and an additive containing more than 3.0 wt.% ZSM-5 on a pure crystal basis on an amorphous support. The patent indicates that although ZSM-5 increases C₃ and C₄ olefins, high temperatures degrade the effectiveness of ZSM-5. Therefore, a temperature of 950°F to 1100° F (510°C to 593°C) in the base of the riser is quenched with light cycle oil downstream of the base to lower the temperature in the riser 10°F-100°F (5.6°C-55.6°C). The ZSM-5 and the quench increase the production of C₃/C₄ light olefins but there is no appreciable ethylene product.

U.S. Patent No. 5,456,821 (Absil) describes catalytic cracking over a catalyst composition which includes large pore molecular sieve, e.g., USY, REY or REUSY and an additive of ZSM-5, in organic oxide binder, e.g., colloidal silica with optional peptidized alumina, and clay. The clay is treated with a phosphorus-containing compound. The clay, source of phosphorus, zeolite and inorganic oxide are slurried together and spray-dried. The catalyst can also contain metal such as platinum as an oxidation promoter. The patent teaches that an active matrix material enhances the conversion. The cracking products included gasoline, and C₃ and C₄ olefins but no appreciable ethylene.

European Patent Specifications Nos. 490,435-B and 372,632-B and European Patent Application No. 385,538-A describe processes for converting hydrocarbonaceous feedstocks to olefins and gasoline using fixed or moving beds. The catalysts described include ZSM-5 in a matrix which includes a large proportion of alumina.

Other types of processes have been developed for producing olefins from paraffinic feeds such as intermediate distillate, raffinate, naphtha and naphthenes, with olefin production directly or indirectly, as described, for example, in U.S. Patent Nos. 4,502,945 (Olbrich), 4,918,256 (Nemet-Mavrodin), 5,171,921 (Gaffney), 5,292,976 (Dessau), and EP 347,003-B. The paraffinic feeds do not contain any significant amount of aromatics. These processes differ not only in feed, but in process conditions, variously including, for example, a requirement for addition of

hydrogen (hydrocracking), use of high space velocities, accepting low conversions per pass and the use of alumina binders for the catalysts. In addition, little coke is produced on the catalyst so that fuel gas must be burned to generate heat for the endothermic reaction. Furthermore, there is no aromatic gasoline range product.

5 Heavy feeds such as resid, vacuum gas oil and atmospheric gas oil which can be processed in the present invention contain more complex components such as aromatics and molecules with large side chains. Processing of heavy feed containing these components generally presents different process considerations and different product.

10 U.S. Patent No. 4,980,053 (Li) describes catalytic cracking (deep catalytic cracking) of a wide range of hydrocarbon feedstocks. Catalysts include pentasil shaped molecular sieves and Y zeolites. Although the composition of the pentasil shape selective molecular sieve (CHP) is not particularly described, a table at column 3 indicates that the pentasil catalyst contains a high proportion of alumina, i.e., 50%
15 alumina, presumably as a matrix. Deep Catalytic Cracking (DCC) is discussed by L.Chapin et al., "*Deep Catalytic Cracking Maximizes Olefin Production*", as presented at the 1994 National Petroleum Refiners Association Meeting. Using a catalyst of unspecified composition, the process produces light olefins of C₃- C₅ from heavy feedstocks. See also, Fu et al., *Oil and Gas Journal*, Jan. 12, 1998, pp. 49-53.

20 The present invention includes a process for catalytically cracking heavy hydrocarbon feed to lighter hydrocarbon products comprising light olefins especially ethylene and propylene, by contacting the feed with a catalyst which comprises ZSM-5 and/or ZSM-11 having a silica/alumina ratio above 12 and bound with a substantially inert matrix material. The contacting is under catalytic cracking conditions. A steam
25 co-feed up to 40 wt.% of the feed, preferably 5 to 20 wt.%, also increases the yield of light olefins. The cracking may also be carried out in the presence of a large pore size zeolite such as a faujasite, e.g. zeolite USY.

The substantially inert matrix material comprises silica, clay or mixtures of these materials. Substantially inert means that the matrix preferably includes less than 10
30 wt.% active matrix material, more preferably less than 5 wt.% active material based on catalyst composition. Active matrix materials are those which have catalytic activity for non-selective cracking and hydrogen transfer. The presence of active matrix material

is minimized in the present invention. While the most commonly used active matrix material for catalyst manufacture is active alumina, the catalyst composition used in the invention preferably includes less than 10 wt.% active alumina, more preferably less than 5 wt.% active alumina, or essentially no active alumina. However, non-
5 acidic forms of alumina such as alpha alumina can be used in the matrix. A small amount of alumina may be used to confer sufficient "hardness" in the catalyst particles for resistance to attrition and high temperatures but without introducing any appreciable non-selective cracking or hydrogen transfer. Preferably, the matrix comprises from zero to 60 wt.% silica and from 50 to 100 wt.% clay.

10 The catalyst composition may optionally include a large pore molecular sieve such as, preferably, the zeolites of the faujasite structure, preferably zeolite USY. When used, faujasites preferably contain less than 2.0 wt.% rare earth (RE) based on faujasite structure. The large pore molecular sieve is also preferably bound with a substantially inert matrix material.

15 The conditions used in the cracking process are selected to minimize hydrogen transfer and it is preferred to avoid hydrogen addition, hydroprocessing and the use of other catalyst components which would introduce excess hydrogen transfer activity. High temperature operation also increases the rate of cracking relative to hydrogen transfer and is therefore preferred. Catalytic cracking conditions typically include a
20 temperature from 510° to 704°C, a pressure from zero up to 8 bar (100 psig), a catalyst/oil ratio from 5 to 30, which corresponds under normal conditions to a WHSV from 1 to 20 hr⁻¹.

The products of the cracking process include gasoline boiling range products and olefins, and preferably less than 10 wt.% light gas product which includes methane,
25 ethane, hydrogen and hydrogen sulfide. Product olefins include ethylene and propylene, preferably in an amount of at least 13 wt.% based on total product; more preferably at least 20 wt.% or 25 wt.% up to 40 wt.% ethylene plus propylene. The gasoline range product is preferably highly aromatic, containing from 20 wt % to 80 wt % BTX (benzene, toluene, xylenes) which are important petrochemical intermediates.

30 The process can be practiced in fluid catalytic cracking (FCC) although moving bed catalytic cracking is possible. A heavy hydrocarbon feed is catalytically cracked in a catalytic cracking reactor operating at catalytic cracking conditions with a catalyst

comprising ZSM-5 and/or ZSM-11 in the substantially inert matrix, optionally with a large pore molecular sieve component, preferably USY. The cracked product effluent includes the desired olefins. During the reaction, coke is formed on the catalyst. The product effluent and the catalyst containing coke are separated from each other and the effluent recovered. The coked catalyst is regenerated by contact with oxygen-containing gas to burn off the coke and produce hot, regenerated catalyst and to produce heat for the endothermic cracking reaction. The hot, regenerated catalyst is recycled to the catalytic cracking reactor. The process produces valuable olefin and aromatic gasoline range products useful as petrochemical feedstocks.

In catalytic cracking, high molecular weight hydrocarbons are converted to lower molecular weight hydrocarbons. The present process provides not only a high quality aromatic gasoline range product, but significantly more light olefins, especially ethylene and propylene. The light olefins of the product can be separated as high quality petrochemical grade and may be used, for example, in the manufacture of valuable polymers such as polyethylene and polypropylene, and in the manufacture of ethers and/or alcohols, and as alkylating agents.

The feedstock, that is, the hydrocarbons to be cracked, typically have a 10% boiling point above 345°C (650°F) and usually a 50% boiling point of at least 750°F (400°C); feeds of this type normally include in whole or in part, gas oils such as vacuum gas oils, coker gas, thermally cracked oils, residual oils, cycle stock, whole top crude, tar sand oil, shale oil, synthetic fuel, heavy hydrocarbon fractions derived from the destructive hydrogenation of coal, tar, pitches, or asphalts, as well as hydrotreated feedstocks derived from any of these stocks. The boiling temperatures specified in this specification are expressed in terms of the boiling point corrected to atmospheric pressure even though the distillation of higher boiling petroleum fractions above 400°C, must be carried out under vacuum in order to avoid thermal cracking. Resids or deeper cut gas oils having an end point of up to 700°C, even with high metals, sulfur or nitrogen contents, can also be cracked using the present catalysts.

Catalytic cracking units which are amenable to the use of the present catalysts normally operate at temperatures from 950°F (510°C) to 1300°F (704°C) preferably from 1000°F (538°C) to 1200°F (649°C) and under atmospheric, or slightly superatmospheric total pressure, usually from zero to 100 psig (1 to 8 bar), preferably

from zero to 50 psig (1 to 4.5 bar). The catalytic process can be either fixed bed, moving bed, transfer line, or fluidized bed, and the hydrocarbon flow can be either concurrent or countercurrent to the catalyst flow. A process according to the invention is particularly applicable to the Fluid Catalytic Cracking (FCC) or the moving bed catalytic cracking processes.

A process according to the invention is particularly applicable to Fluid Catalytic Cracking. In fluidized catalytic cracking processes, the fluidizable catalyst is a fine powder of 20 to 140 micrometers. This powder is generally suspended in the feed and propelled upward in a reaction zone. Diluent such as steam up to 40% may be added to the feed at the bottom of the riser to lower hydrocarbon partial pressure. A heavy hydrocarbon feedstock, e.g., a gas oil, is admixed with a suitable cracking catalyst to provide a fluidized suspension and cracked in an elongated reactor or riser, at elevated temperatures to provide a mixture of lighter hydrocarbon products. The gaseous reaction products and spent catalyst are discharged from the riser into a separator, e.g. a cyclone unit, located within the upper section of an enclosed stripping vessel, or stripper, with the reaction products being conveyed to a product recovery zone and the spent catalyst entering a dense catalyst bed within the lower section of the stripper. In order to remove entrained hydrocarbons from the spent catalyst, prior to conveying the latter to a catalyst regenerator unit, an inert stripping gas, e.g., steam, is passed through the catalyst bed where it absorbs such hydrocarbons conveying them to the product recovery zone. The spent catalyst includes deposited coke which is burned off in an oxygen-containing atmosphere in a regenerator to produce hot, regenerated catalyst. The fluidizable catalyst is continuously circulated between the riser and the regenerator and serves to transfer heat from the latter to the former thereby supplying the thermal needs of the cracking reaction which is endothermic. The FCC conversion conditions typically include a temperature from 950°F (510°C) to 1250°F (677°C), preferably 1000°F (538°C) to 1200°F (649°C); catalyst/oil weight ratio from 5 to 30, preferably from 5 to 20; a catalyst riser residence time (contact time), of 0.5 to 10 seconds, preferably 1 to 5 seconds; and a weight hourly space velocity (WHSV) of 1 to 20 hr⁻¹, preferably 5 to 15 hr⁻¹.

ZSM-5/ZSM-11 Zeolite Component

The catalyst composition includes an intermediate pore zeolite component which is ZSM-5 (U.S. Pat. No. 3,702,886 and Re. 29,948) and/or ZSM-11 (U.S. Pat. No. 3,709,979). More preferred is ZSM-5. Preferably, relatively high silica zeolites ZSM-5 or ZSM-11 are used, i.e., those with a silica/alumina molar ratio above 5, and more preferably with a ratio of 12, 20, 70, 100, 500 or higher, even more preferably 12 to 100. This ratio is meant to represent, as closely as possible, the molar ratio in the rigid framework of the zeolite crystal and to exclude silicon and aluminum in the matrix or in cationic or other form within the channels. Other metals besides aluminum have been incorporated into the zeolite framework such as gallium which can be used in the invention. The preparation of the zeolite may require reduction of the sodium content, as well as conversion to the protonated form. This can be accomplished, for example by employing the procedure of converting the zeolite to an intermediate ammonium form as a result of ammonium ion exchange followed by calcination to provide the hydrogen form. The operational requirements of these procedures are well known in the art. The source of the ammonium ion is not critical; thus the source can be ammonium hydroxide or an ammonium salt such as ammonium nitrate, ammonium sulfate or ammonium chloride. Calcination of the ammonium exchanged zeolite will produce its hydrogen form. Calcination can be effected at temperatures up to 550°C.

The intermediate pore zeolite may be stabilized with phosphorus. Phosphorus stabilization is well known and is described, for example, in U.S. Patent Nos. 3,911,041 to Kaeding et al., 3,972,832 to Butter et al., 4,423,266 to Young et al., 4,590,321 to Chu, and 5,456,821 to Absil et al. The phosphorus can be added in an amount of zero to 10 wt.% of the total catalyst composition, preferably from 1 to 8 wt.%.

In addition to the ZSM-5 and/or ZSM-11 zeolite component, the catalyst composition may optionally include a large pore molecular sieve component with cracking activity. The large-pore molecular sieve component of the catalyst composition may comprise any active component which has cracking activity and which has a pore opening of greater than 0.7 nm in effective diameter. The active component may be a conventional large-pore zeolite molecular sieve X (U.S. Pat. No. 2,882,244); REX; zeolite Y (U.S. Pat. No. 3,130,007); Ultrastable Y (USY) (U.S. Pat. No. 3, 449,070); Rare Earth exchanged Y (REY) (U.S. Pat. No. 4,415,438); Rare

Earth exchanged USY (REUSY); Dealuminated Y (DeAl Y) (U.S. Pat. Nos. 3,442,792 and 4,331,694); Ultrahydrophobic Y (UHPY) (U.S. Pat. No. 4,401,556); and/or dealuminated silicon-enriched zeolites, e.g., LZ-210 (U.S. Pat. No. 4,678,765). Preferred are higher silica forms of zeolite Y. ZSM-20 (U.S. Pat. No. 3,972,983);
5 zeolite Beta (U.S. Pat. No. 3,308,069); zeolite L (U.S. Pat. Nos. 3,216,789 and 4,701,315). Naturally occurring zeolites such as faujasite, mordenite may also be used. These materials may be subjected to conventional treatments, such as impregnation or ion exchange with rare earths to increase stability.

10 In current commercial practice most cracking catalysts contain these large-pore zeolite molecular sieves. Other large-pore crystalline molecular sieves include pillared silicates and/or clays; aluminophosphates e.g., $\text{ALPO}_4\text{-5}$, $\text{ALPO}_4\text{-8}$, VPI-5; silicoaluminophosphates, e.g., SAPO-5, SAPO-37, SAPO-40, MCM-9; and other metal aluminophosphates. Mesoporous crystalline material for use as the molecular sieve includes MCM-41. These are variously described in U.S. Pat. Nos. 4,310,440;
15 4,440,871; 4,554,143; 4,567,029; 4,666,875; 4,742,033; 4,880,611; 4,859,314, 4,791,083; 5,102,643; and 5,098,684. The large-pore molecular sieve catalyst component may include phosphorus or a phosphorus compound for any of the functions generally attributed thereto, such as, for example, attrition resistance, stability, metals passivation, and coke reduction.

20 The preferred large-pore molecular sieve are zeolites of the faujasite structure with a silica/alumina ratio greater than 2, preferably a zeolite Y, more preferably USY. In a preferred embodiment, the large pore molecular sieve contains less than 2.0 wt.% rare earth, preferably less than 1.0 wt. % rare earth (RE) based on faujasite, e.g., 0.3 wt % RE.

25 To prepare the large-pore molecular sieve component for use, a slurry may be formed by deagglomerating the molecular sieve, preferably in an aqueous solution. A slurry of the matrix material may be formed by mixing the desired matrix components such as clay and/or inorganic oxide in an aqueous solution. The molecular sieve slurry and the matrix slurry are then well mixed and spray dried to form catalyst
30 particles of, for example, less than 200 micrometers in diameter. The large pore molecular sieve can be prepared in particles separately from the ZSM-5 and/or ZSM-11 or together in the same particle with the ZSM-5 and/or ZSM-11. When the large

pore molecular sieve is bound in particles separate from the ZSM-5 and/or ZSM-11, the binder matrix for the large pore molecular sieve is preferably substantially inert, containing, e.g., little if any active alumina, e.g., less than 10 wt.% active alumina, preferably less than 5 wt.% active alumina.

5 On a pure crystal basis, the catalyst composition preferably comprises from 1 wt.% to 50 wt % of the intermediate pores size component (ZSM-5 and/or ZSM-11) and, when used, from 1 wt.% to 50 wt % of the large-pore molecular sieve component. More preferably, the ratio of the large-pore molecular sieve/intermediate pore zeolite (ZSM-5 and/or ZSM-11) on a pure crystal basis is from 10:1 to 1:10.

10 Matrix

For use in catalytic conversion processes a zeolite is usually compounded with a binder or matrix material, generally inorganic oxides, for increased resistance to temperatures and other conditions, e.g., mechanical attrition, which occur in various hydrocarbon conversion processes such as cracking. It is generally necessary for the catalysts to be resistant to mechanical attrition, that is, the formation of fines which are small particles, e.g., less than 20 micrometer.

The matrix materials used in the present compositions are substantially inert, implying that the catalyst composition includes less than 10 wt.%, preferably less than 5 wt.%, active material. The most commonly used active material is alumina in its active form. Active alumina is generally made by peptidizing a dispersable alumina (e.g., formed from the Bayer process or by controlled hydrolysis of aluminum alcoholates) with acid (e.g., formic, nitric). The dispersed alumina slurry is then mixed into the matrix. However, the present catalyst composition includes less than 10 wt.%, preferably less than 5 wt.%, active alumina.

25 Matrix materials particularly useful for the present catalyst compositions include silica and clay. Procedures for preparing silica bound ZSM-5 are described, e.g., in U.S. Patent Nos. 4,582,815, 5,053,374 and 5,182,242. The matrix can be in the form of a cogel or sol. A mixture of these components can also be used. The sol can comprise zero to 60% by weight of the matrix. Preferably, the matrix comprises 50 to 100 wt.% clay, and zero to 50 wt.% sol. The matrix can comprise up to 100% by weight clay. Naturally occurring clays which can be composited with the catalyst include the montmorillonite and kaolin families which include the subbentonites, and

the kaolins. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification. Clay is generally used as a filler to produce denser catalyst particles. In addition to the foregoing materials, catalyst can be composited with a porous matrix material such as silica-magnesia, silica-zirconia, silica-magnesia-zirconia.

When the ZSM-5 and/or ZSM-11 is bound separately from the large pore molecular sieve, the relative proportions of finely divided zeolite component and inorganic oxide matrix can vary widely, with the molecular sieve content ranging from 1 to 90 percent by weight, and more usually from 2 to 80 weight percent of the composite. Preferably, the zeolite makes up 5 to 75 wt. % of the catalyst and the matrix makes up 25 to 95 wt.% of the catalyst.

The total catalyst composition preferably comprises the large pore molecular sieve in an amount of 1 to 50 wt.%, preferably 10 to 40 wt. %; ZSM-5 and/or ZSM-11 in an amount of 1 to 50 wt %, preferably 10 to 40 wt.%; and matrix material in an amount of zero to 80 wt.%, preferably 20 to 60 wt.%. It is important to exclude catalyst components which could introduce excess hydrogen transfer activity such as rare earth stabilized faujasite, large amounts of active alumina or metals, such as platinum, palladium, rare earth, tin, etc., which supply an undesirable hydrogenation-dehydrogenation function.

The products of the catalytic cracking include gasoline range product and light olefins. The gasoline range product preferably includes from 20 wt.% to 80 wt.% aromatics BTX (benzene, toluene, xylenes), preferably greater than 40 wt.% BTX. The product also includes ethylene, e.g., over 1 wt.% ethylene or at least 2 or 3 wt.% ethylene. In favorable cases, the product includes greater than 5 wt.% ethylene, and it is possible to achieve greater than 8 wt.% ethylene, as a percentage of the feed based on the total product. A substantial amount of propylene is also produced, and the amount of ethylene plus propylene may be greater than 13 wt.% or 15 wt % of the feed based on total product. Ethylene plus propylene yields of greater than 20 wt.% or higher are possible, for example, greater than 25 wt.% (same basis). Small amounts of light gas components including methane, ethane, hydrogen and hydrogen sulfide are also produced, e.g., less than 10 wt.%. From another point of view, the product can include preferably less than 10 wt.% dry gas (methane, ethane, hydrogen,

hydrogen sulfide and ethylene). At least 50% of dry gas product is ethylene. The hydrocarbon conversion is from 50% to 95% of the feed, preferably 65% to 90%. The amount of coke produced generally increases with conversion conditions.

The following non-limiting examples illustrate the invention. In the following examples, prior to testing all catalysts were calcined in air at 1000°F (648°C) for 3 hours in a fixed bed with a heating at a rate of 5F (2.8C) per minute to 1000°F (648°C). Except where an unsteamed catalyst is specified in the examples, the calcined catalysts were steamed in a 20 hour cyclic propylene steaming in a fluid bed at 1435°F (780°C) and 50 psig (4.4 bar), 50% steam to simulate use under FCC conditions. In cyclic propylene steaming, 5 minute cycles of N₂, air, N₂ are continuously performed for the length of the steaming.

EXAMPLE 1

Catalysts were prepared as follows with properties shown in Table 1 below:

15 Catalyst A

A conventional FCC catalyst sampled from a refinery consisted of 35 wt.% rare earth exchanged ultrastabilized faujasite (REUSY) in a silica sol matrix (Davison, MRO-35+) with a small amount of matrix activity.

Catalyst B

20 This catalyst consisted of 40 wt % ZSM-5 (23:1 SiO₂/Al₂O₃), 30% clay, 5% peptidized alumina, 25% silica sol. In addition, phosphorus (2.3 wt.% on finished catalyst) was added to the spray dryer slurry. The slurry containing all the catalyst components was spray dried.

Catalyst C

25 This catalyst consisted of 40 wt.% ZSM-5 (55:1 SiO₂/Al₂O₃) in an alumina sol matrix.

TABLE 1

	Catalyst A	Catalyst B	Catalyst C
Description	Equilibrium Catalyst, 35% REUSY in silica sol matrix	40% ZSM-5, P-stabilized, 30% clay, 5% Al ₂ O ₃ 25% silica	40% ZSM-5 in Al ₂ O ₃ sol matrix
SiO ₂ wt%	54.2	68.7	61.2
Al ₂ O ₃ wt%	34.4	22.8	39.2
Na wt%	0.33	0.11	0.15
P wt%	0	2.3	0.2
Rare Earth Oxide, wt%	3.0	0	0

EXAMPLE 2

5 The catalysts prepared in Example 1 were used in a fixed-fluid-bed unit to process a mid Continent type Heavy Gas Oil with the properties listed in Table 2.

TABLE 2

API Gravity @ 60°C	19.7
Sulfur, wt%	2.6
Nitrogen, ppmw	1500
Basic Nitrogen, ppmw	480
Carbon, wt%	85.1
Hydrogen, wt%	12.3
Avg. Molecular Wt., gm/mole	369
Distillation (D1160) IBP, °F	497 (258°C)
10 vol%, °F	677 (358°C)
50 vol%, °F	826 (441°C)
90 vol%, °F	1001 (538°C)
FBP, °F	1025 (552°)

The catalyst (225 gms) was charged to a quartz reactor and heated to reaction temperature. Feed oil was added at 44gm/min to give a WHSV of 12. The gas phase residence time was 0.5 to 1 second. Experiment duration was varied from 20 seconds to 90 seconds to vary the overall catalyst to oil weight ratio between 2 and 24. Liquid products were collected in a series of traps, and the gas was collected in a vessel that was evacuated prior to the run. At the end of the run, the traps were weathered to room temperature and the gas was analyzed by Gas Chromatography. The liquid product (syncrude) was analyzed by Gas Chromatography to allow calculation of gasoline, LFO (light fuel oil), and HFO (heavy fuel oil) yields (ASTM D 2887-97). The product was also analyzed by GC (Gas Chromatography) to identify C5- components. Runs with several catalyst/oil ratios between 1080°F (582°C) and 1200°F (649°) were done over the three catalysts. Based on this, yields at constant conversion were interpolated. The reaction temperatures, conversion levels, catalyst/oil (C/O) ratios and products are listed in Table 3 below.

TABLE 3

	35% REUSY/silica matrix	sol	40% ZSM-5 P-stabilized 30% clay 5% Al ₂ O ₃ 25% Silica	40% ZSM-5 Al ₂ O ₃ matrix	sol
Catalyst	Catalyst A	Catalyst A	Catalyst B	Catalyst C	
Temperature, °F	1080 (582°C)	1200 (650°)	1200 (650°C)	1200 (649°C)	
Conversion, vol%	72	72	67	67	
C/O, gm/gm	3.5	2.4	23.0	7.5	
H ₂ , wt%	0.31	0.34	0.30	0.38	
H ₂ S, wt%	1.87	1.83	0.9	1.39	
C1, wt%	1.6	2.7	3.5	3.4	
C2, wt%	1.2	2.2	3.2	2.5	
C2=, wt%	1.0	1.6	7.6	3.5	
C3, wt%	1.6	1.9	2.4	1.7	
C3=, wt%	5.3	5.9	13.7	11.7	
C4, wt%	3.6	2.4	0.9	1.0	
C4=, wt%	6.3	6.2	7.8	9.8	
C5, wt%	4.4	2.7	0.3	0.4	
C5=, wt%	6.3	6.3	2.6		
C5+ gaso. wt%	41.0	38.3	17.9	20.4	
LFO, wt%	21.2	20.8	18.5	20.6	
HFO, wt%	9.7	10.4	16.4	14.9	
Coke, wt%	5.2	5.4	7.0	8.9	

The yields for catalysts B and C are estimated at 67 vol% conversion. For Catalyst B, the gasoline yield over this catalyst was half that of conventional FCC, and the gasoline quality is expected to be very aromatic with high octane. Achieving these high yields of light olefins in one aspect depends on the zeolite/matrix balance. This is seen in the results of Catalyst C. Because of the high matrix activity, a C/O of 7.5 is sufficient to achieve 67 vol% conversion. However, the yield of ethylene and propylene were 3.5 and 11.7 respectively, less than obtained over Catalyst B. At the conversion range studied, the zeolite to matrix balance in Catalyst C appears less favorable than that of Catalyst B for obtaining high ethylene and propylene yields. The yield is seen to be primarily a function of conversion and not of temperature. This indicates that the ethylene is produced by catalytic cracking and not by thermal cracking. In this work, the gas residence time has been held constant. It is expected that similar yields could be obtained by increasing the gas residence time and lowering either temperature or catalyst/oil ratio.

EXAMPLE 3

The following catalysts were prepared:

Catalyst D

This catalyst consisted of ZSM-5 (silica/alumina ratio of 450/1) formulated like Catalyst B (40% ZSM-5, 30% clay, 5% peptidized alumina, 25% silica sol, stabilized with phosphorus).

Catalyst E

This catalyst consisted of ZSM-5 in silica sol and clay with no alumina in the binder, stabilized with phosphorus, prepared as was Catalyst B but without the peptidized alumina.

Catalyst F

This catalyst consisted of ZSM-11 prepared as was Catalyst B with 40% ZSM-11 stabilized with phosphorus, with 30% clay, 5% peptidized alumina, 25% silica sol.

Catalyst G

This catalyst consisted of ZSM-5 prepared as were Catalysts B and E but with 20% peptized alumina.

Catalysts B, D, and F were used in a fixed-fluid-bed unit to process a Sour Heavy Gas Oil Feed. Process conditions included a temperature of 1200°F (650°C) and a WHSV of 12. The results are shown in Table 4 below.

5

TABLE 4

	40% ZSM-5 30% clay 5% Al ₂ O ₃ , 25% silica	40% high silica ZSM-5, 30% clay 5% Al ₂ O ₃ 25% silica	ZSM-11, 30%clay, 5% Al ₂ O ₃ , 25% silica
Catalyst	B	D	F
Conversion, wt%	60	60	60
Cat./Oil	14.3	23.9	10.4
C2-, wt%	7.13	9.42	6.93
C2=, wt%	6.7	5.5	5.7
C3=, wt%	12.7	10.7	12.4
C3, wt%	2.1	1.6	1.7
C2+=C3=,wt%	19.4	16.2	18.1
C4=, wt%	7.3	7.7	6.7
C4, wt% 1.2	0.8	0.5	
Gasoline wt%, C5-430°F (220°C)	17.8	17.8	19.9
LFO, wt%	19.8	18.8	20.2
HFO, wt%, 700°F+ (370°C+)	20.2	21.2	19.8
Coke, wt%	5.51	6.73	5.35

The results demonstrate that ethylene yield is related to the total ZSM-5 activity. ZSM-11 is also effective.

5 **EXAMPLE 4**

Three ZSM-5-containing catalysts G, B and E, respectively with 20%, 5% and zero alumina in the binder matrix, were used to process heavy feed as in Example 3. Catalyst composition and conversion results are summarized in Table 5.

TABLE 5

Catalyst (ZSM-5)		G		B		E
Si/Al ₂ (mol/mol)		26		26		26
SiO ₂ , wt% (P-free)		10		25		30
Al ₂ O ₃ , wt% (P-free)		20		5		0
P, wt%		3		2.7		3
Temperature, °F		1200 (650°C)		1200 (650°C)		1200 (650°)
WHSV		12		12		12
Cat/Oil		9.4		14.3		
13.8						
430°F+ (220°C+) Conversion, wt%		60		60		60
C ₂ -, wt%		3.1		5.8		6.1
C ₂ =, wt%		3.9		6.7		7.7
C ₃ =, wt%		12.7		12.7		13.3
C ₃ , wt%		2.2		2.1		2.6
C ₂ =+C ₃ =, wt%		16.6		19.4		21
C ₄ =, wt%		8.3		7.3		7
C ₄ , wt%		0.8		0.8		0.9
Gasoline wt%, C ₅ -430°F (220°C)		19.5		17.8		16.8
LCO, wt%		23.1		19.8		19.9
HFO, wt%, 700°F+ (370°C+)		16.9		20.2		20.1
Coke, wt%		6.81		5.51		4.39

The results in Table 5 indicate that the less alumina in the binder, the higher the ethylene yield. The ethylene yield increased from 3.9% to 6.7% to 7.7% as the alumina content in the matrix decreased from 20% to 5% to 0%. The propylene yields remained relatively constant at 12.7%, 12.7% and 13.3%. It appears that achieving these high yields of light olefins depends on the zeolite/matrix balance as well as the acidity of the matrix. At the conversion range studied, Catalyst E with no matrix acidity appears more favorable than that of Catalysts B and G for obtaining high ethylene yields. Results in Table 5 also suggest that less coke is produced when there is no alumina in the binder.

The gas residence time was held constant in all of the cases shown in Table 5, and the reaction temperature was 1200° F (650°). It is expected that similar yields could be obtained by increasing the gas residence time and lowering either temperature or catalyst:oil ratio.

Although ethylene is a product of thermal-cracking, Table 4 and 5 shows that ethylene yield strongly depends on the nature of the catalysts at a constant reaction temperature, which indicates that the ethylene is produced here by catalytic cracking and not by thermal cracking.

EXAMPLE 5

Catalyst blends were prepared containing from zero to 100 wt% Catalyst H and a complementary amount of Catalyst I. Catalyst H was a standard cracking catalyst (Octacat™) including 40 wt% USY in a silica sol and clay matrix with no phosphorus. Catalyst I was 40% ZSM-5 (26:1 silica/alumina) in a silica sol matrix with 5% alumina (derived from pseudoboemite) and clay, phosphorus stabilized. The catalyst blends were used in a fixed-fluid-bed unit to process a Mid Continent type heavy gas oil feed (Table 6) at 1200°F (650°C) and a WHSV of 12. Results are in Table 7.

TABLE 1

API Gravity @ 60°C	19.7
Sulfur, wt%	2.6
Nitrogen, ppmw	1500
Basic Nitrogen, ppmw	480
Carbon, wt%	85.1
Hydrogen, wt%	12.3
Avg. Molecular Wt., gm/mole	369
Distillation (D1160) IBP, °F	497 (258°C)
10 vol%, °F	677 (358°C)
50 vol%, °F	826 (441°C)
90 vol%, °F	1001 (538°C)
FBP, °F	1025 (552°C)

TABLE 7

Catalyst	0%H/ 100%I	10%H /90%I	30%H / 70%I	50%H/ 50%I	70%H/ 30%I	100%H/ 0%I
Conversion, Wt%	70.0					
Cat/Oil	22.0	22.0	15.2	7.7	4.9	4.9
C2-, wt% C2=, wt%	8.9 8.5	5.9 7.7	5.8 7.0	4.8 6.0	4.8 5.3	7.9 2.6
C3=, wt% C3, wt%	14.3 3.1	15.8 2.6	17.1 2.4	16.3 2.3	15.6 2.2	7.3 1.9
C2+=C3=, wt%	22.8	23.5	24.1	22.3	20.9	9.9
C4=, wt% C4, wt%	7.1 1.1	8.7 1.1	9.3 1.2	10.2 1.8	9.5 1.6	8.2 1.9
Gasoline wt% C5-430°F (221°C)	18.9	18.3	19.9	22.9	25.2	35.4
LFO, wt%	16.7	16.3	16.8	19.6	19.1	19.9
HFO, wt%, 700°F+ (370°C+)	13.3	13.7	13.2	10.4	10.9	10.1
Coke, wt%	8.1	8.4	6.0	4.1	4.4	4.7

- 5 The data in Table 7 demonstrate that ZSM-5 with a substantially inert matrix showed high ethylene yields, while the presence of large pore catalyst improved activity as interpreted by the lower catalyst/oil ratio needed for a 70 wt.% conversion.

EXAMPLE 6

50-50 catalyst blends were prepared containing 50 wt.% USY-containing Catalyst H described in Example 5 and 50 wt.% each of the following:

- 1.) phosphorus stabilized ZSM-11(40% ZSM-11 in a silica sol matrix with 5%
5 alumina and clay, P-stabilized);
- 2.) ZSM-5-containing Catalyst B described in Example 5 (40% ZSM-5 in a silica
sol matrix with 5% alumina and clay, P-stabilized);
- 3.) phosphorus stabilized ZSM-5 in a silica sol and clay binder matrix with no
alumina in the binder designated Catalyst J.

10 The catalyst blends were used to process a gas oil feed as described in Example
5. The results are shown in Table 8.

TABLE 8

Catalyst, 50/50 Catalyst H and	(5% alumina) P-ZSM-11	(5% alumina) Catalyst I	(No alumina) Catalyst J
Conversion, Wt%	75.0		
Cat/Oil	16.0	15.9	10.0
C2-, wt% C2=, wt%	8.3 6.1	7.6 6.9	6.7 8.4
C3=, wt% C3, wt%	16.4 2.4	17.0 2.8	16.1 3.0
C2+=C3=, wt%	22.5	23.9	24.5
C4=, wt% C4, wt%	10.0 2.1	9.8 2.0	8.5 1.9
Gasoline wt% C5-430°F (C5-220°C)	22.4	21.2	25.7
LFO, wt%	13.6	14.3	13.4
HFO, wt%, 700°F+ (370°C+)	11.4	10.8	11.4
Coke, wt%	7.8	7.7	4.9

The results demonstrate that a catalyst with no alumina in the matrix produces the highest ethylene yields and the highest ethylene plus propylene yields. Also, the catalyst with no active alumina gave a lower coke yield, and ZSM-5 and ZSM-11 were both effective.

EXAMPLE 7

Blends were prepared of 70 wt.% USY containing Catalyst H (40% USY in a silica sol matrix with no phosphorus) and 30 wt.% ZSM-5-containing Catalyst I. In one blend, Catalyst I was pre-steamed using the cyclic propylene steaming described

above and in another blend, Catalyst I was calcined for 3 hours in air as previously described but otherwise not steamed. The blends containing steamed and unsteamed Catalyst I were used in fixed-fluid-bed unit to process a Sour Heavy Gas Oil Feed at 1200°F (649°C), and a WHSV of 12. The results are shown in Table 9.

5

TABLE 9

Catalyst	70% Catalyst H 30% Catalyst I	70% Catalyst H 30% Catalyst I
Catalyst I Pre-treatment	Steamed	Unsteamed
Conversion, Wt%	75.0	
Cat/Oil	12.9	8.6
C2-, wt% C2=, wt%	7.6 6.5	7.6 9.2
C3=, wt% C3, wt%	16.6 2.8	14.3 3.8
C2+=C3=, wt%	23.1	23.5
C4=, wt% C4, wt%	9.4 2.3	7.1 2.0
Gasoline wt% C5-430°F (221°C)	22.8	25.5
LFO, wt%	15.9	16.1
HFO, wt%, 700°F+ (370°C+)	9.1	8.9
Coke, wt%	7.0	5.5

The results show that the unsteamed catalyst increased ethylene yield and gasoline range product, demonstrating that the ethylene is produced catalytically not thermally.

10

EXAMPLE 8

The 70% Catalyst H /30% steamed Catalyst I catalyst blend prepared in Example 3 was tested both in a fixed-fluid-bed and a riser processing the same Mid Continent gas oil feed given in Table 6. The process conditions and results are shown in Table 10.

TABLE 10

Catalyst	70% Catalyst H/ 30% Catalyst I	70% Catalyst I/ 30% Catalyst I
Test Unit	FFB	Riser
Conversion, Wt%	75.0	
Cat/Oil Temperature, °F Pressure, psig (bar)	12.9 1190 (645°C) ~0 (~1)	12.9 1140 (615°C) 20.0 (~2.4)
C2-, wt% C2=, wt%	7.6 6.5	8.5 5.6
C3=, wt% C3, wt%	16.6 2.8	13.8 2.4
C2+=C3=, wt%	23.1	19.4
C4=, wt% C4, wt%	9.4 2.3	8.8 1.7
Gasoline wt% C5-430°F (C5-220°C)	22.8	30.1
LFO, wt%	15.9	12.1
HFO, wt%, 700°F+ (370°C+)	9.1	12.7
Coke, wt%	7.0	4.3

The data in Table 10 demonstrate that similar results are obtained in a fixed-fluid-bed and a riser.

EXAMPLE 9

A blend was prepared of 50 wt.% USY-containing Catalyst H and 50 wt.% ZSM-5-containing Catalyst I. Another blend was prepared of 50 wt.% USY-containing Catalyst H and 50 wt.% ZSM-5-containing Catalyst J (no alumina). The blends were used in a fixed-fluid-bed under conditions described in Example 1 but with 7.5 wt.% H₂O cofeed. In another run, 15 wt.% water co-feed was added to the feed. Results are shown in Table 11.

TABLE 11

Catalyst, 50/50 Catalyst H (USY)	Catalyst I (ZSM-5)	Catalyst J (ZSM-5) (no alumina)
Conversion, Wt%	75.0	
Cat/Oil H ₂ O Co-feed, wt%	8.6 7.5	11.4 7.5/15
C2-, wt% C2=, wt%	7.6 9.6	6.2 10.3
C3=, wt% C3, wt%	17.0 2.7	18.5 2.8
C2+=C3=, wt%	26.6	28.8
C4=, wt% C4, wt%	7.9 1.4	8.6 1.9
Gasoline wt% C5-430°F (220°C)	22.8	22.5
Coke, wt%	6.3	4.4

When compared with the results in Table 9, the results in Table 11 show that including water in the feed improves ethylene yield and ethylene plus propylene yield. The results also confirm that a catalyst with an inert matrix provides higher yields of lower olefins.

EXAMPLE 10

A catalyst blend was prepared containing 50 wt.% USY-containing Catalyst H and 50 wt.% ZSM-5-containing catalyst J (no alumina). The USY/ZSM-5 blend was used
5 to process a paraffinic 760°F+ (405°C+) resid. Feed properties and results are summarized in Table 12 below. Table 12 also compares conversion results described by Fu et al., *Oil & Gas Journal*, Jan. 12, 1998, pp 49-53 for Deep Catalytic Cracking. The Fu et al. catalyst is thought to contain rare earth (RE) ZSM-5 (pentasil) to process hydrotreated paraffinic feed.

TABLE 12

Feed	Paraffinic Resid	Hydrotreated Paraffinic Feed
Gravity, API Refractive Index, 75°C Distillation IBP °F(°C) 10% 50% EP	28.41 619 (326°C) 717 (381°C) 827 (442°C) 1342 (728°C)	31.40 1.469 315 (157°C) 649 (343°C) 806 430°C) 1076 (580°C)
Catalyst	50% Catalyst H 50% Catalyst J	ZRP-1 (ZSM-5)
H ₂ O Cofeed, wt% on Feed	15/7.5	~22
Conversion, Wt%	82	
C2-, wt% C2=, wt%	5.9 12.3	5.2 5.1
C3=, wt% C2+=C3, wt%	20.9 33.2	17.4 22.5
C4=, wt% C3+C4 Paraffins, wt%	10.7 8.6	11 11.6
Gasoline wt%, C5-430°F (C5-220°C)	21.4	31.9
Coke, wt%	3.6	~6.0

The results demonstrate that higher amounts of lower olefins ethylene and
 5 ethylene plus propylene are produced by the use of the present catalysts.

CLAIMS:

1. A process for catalytically cracking heavy hydrocarbon feed to products lighter than the feed with enhanced yield of light olefins, which comprises contacting the feed under catalytic cracking conditions with a catalyst which comprises ZSM-5 and/or ZSM-11 as a zeolite component and a substantially inert matrix material.

2. A process according to claim 1 in which the zeolite comprises 5 to 75 wt.% of the catalyst and the matrix material comprises 25 to 95 wt.% of the catalyst.

3. A process according to claim 1 in which the matrix material comprises less than 10 wt.% active matrix material based on total catalyst composition. And comprises silica, clay or mixtures of silica and clay.

4. A process according to claim 3 in which the matrix material comprises less than 10 wt.% active alumina.

5. A process according to claim 1 in which the catalyst also comprises a large pore size molecular sieve cracking component.

6. A process according to claim 5 in which the large pore molecular sieve component makes up 5 to 50 wt.% of the catalyst, the ZSM-5 and/or ZSM-11 zeolite component makes up 5 to 50 wt.% of the catalyst and matrix material makes up 5 to 90 wt.% of the catalyst.

7. A process according to claim 5 in which the large pore molecular sieve component comprises USY containing less than 2.0 wt.% rare earth cations on a large pore molecular sieve crystal basis.

8. A process according to Claim 1 in which water is added to the feed in an amount up to 40 wt.% of the feed.

9. A process according to claim 1 in which the product of the catalytic cracking comprises light olefins and gasoline range product, said gasoline range product comprising from 20 wt.% to 80 wt.% benzene/toluene/xylene and the light olefins comprise ethylene and propylene in an amount greater than 13 wt.% based on total
5 product.

10. A process according to claim 1 in which the catalytic cracking conditions comprise a temperature from 510°C to 704°C, a pressure up to 8 bar, a catalyst/oil weight ratio from 5 to 30, and a WHSV from 1 to 20 hr⁻¹.

INTERNATIONAL SEARCH REPORT

International application No.
PCT US99 27137

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C10G 11/02, 11/05

US CL : 208/113, 118, 120.01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/113, 118, 120.01

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,957,617 A (OWEN ET AL) 18 September 1990 (18-09-90), see col. 2, lines 1-22 and 33-66; col. 3, lines 37-63; col. 5, lines 16-22; and col. 6, lines 3-63.	1-10
X	US 4,929,337 A (HERBST ET AL) 29 May 1990 (29-05-90), see col. 1, lines 36-58 and col. 4, line 55 through col. 12, line 43.	1-10
A	US 5,788,834 A (LAPINSKI) 04 August 1998 (04-08-98).	1-10
A	US 5,318,696 A (KOWALSKI) 07 June 1994 (07-06-94).	1-10
A	US 5,055,176 A (HERBST ET AL) 08 October 1991 (08-10-91).	1-10

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

10 JANUARY 2000

Date of mailing of the international search report

02 FEB 2000

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INTERNATIONAL SEARCH REPORT

International application No.
PCT US99 27137

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,006,497 A (HERBST ET AL) 09 April 1991 (09-04-91).	1-10
A	US 4,614,578 A (CHESTER ET AL) 30 September 1986 (30-09-86).	1-10
A	US 3,758,403 A (ROSINSKI ET AL) 11 September 1973 (11-09-73).	1-10
A	US 449 H (RUDESILL) 01 March 1988 (01-03-88).	1-10